

HIGH BREAKDOWN STRENGTH, MULTILAYER CERAMICS FOR COMPACT PULSED POWER APPLICATIONS

W. Huebner, S.C. Zhang, B. Gilmore
University of Missouri-Rolla, Rolla, Missouri, USA

M.L. Krogh, B.C. Schultz
AlliedSignal FM&T, * Kansas City, Missouri, USA

R. C. Pate, L. F. Rinehart, J. M. Lundstrom
Sandia National Laboratory, New Mexico, USA

Abstract

Advanced ceramics are being developed for use in large area, high voltage devices in order to achieve high specific energy densities ($>10^6 \text{ J/m}^3$) and physical size reduction. Initial materials based on slip cast TiO_2 exhibited a high bulk breakdown strength (BDS $>300 \text{ kV/cm}$) and high permittivity with low dispersion ($\epsilon \approx 100$). However, strong area and thickness dependencies were noted. To increase the BDS, multilayer dielectric compositions are being developed based on glass/ TiO_2 composites. The addition of glass increases the density ($\approx 99.8\%$ theoretical), forms a continuous grain boundary phase, and also allows the use of high temperature processes to change the physical shape of the dielectric. The permittivity can also be manipulated since the volume fraction and connectivity of the glassy phase can be readily shifted. Results from this study on bulk breakdown of TiO_2 multilayer structures with an area of 2cm^2 and 0.1cm thickness have measured 650 kV/cm . Furthermore, a strong dependence of breakdown strength and permittivity has been observed and correlated with microstructure and the glass composition. This paper presents the interactive effects of manipulation of these variables.

I. INTRODUCTION

Dielectrics for pulsed power applications need to satisfy several key material and processing parameters [1], including a high voltage hold off ($\geq 300 \text{ kV}$), a high, nondispersive permittivity ($\epsilon \approx 100$ to 400), surface flashover inhibition at the edge, the ability to be triggered by surface flashover switching, and the ability to be fabricated into various shapes and sizes.

Higher voltages and permittivities result in greater stored energy density and hence smaller systems. Current systems based on water dielectrics can hold off $\approx 150 \text{ kV/cm}$, have a $\epsilon \approx 80$, and are self-healing [1]. Their replacement by a solid system such as a polymer or ceramic is highly desirable, but currently available systems based on polymers [2] or ceramics [3] are insufficient due to fundamental shortcomings.

This work focused on improving the microstructure and composition of ceramic-based systems, with particular emphasis on increasing the BDS and ϵ . The primary source of voltage failure for a ceramic is related

to the presence of porosity [4,5], and the associated field/stress amplification. By adding a high BDS, low ϵ glass to a higher ϵ dielectric, the porosity can be virtually eliminated, and the BDS is increased. Here we report on studies on glass-loaded TiO_2 dielectrics, with additional improvements in processing methodology.

II. EXPERIMENTAL PROCEDURE

In this work TiO_2 (HG TICON, TAM Ceramics, NY) was used as the base dielectric. TiO_2 has a nondispersive $\epsilon \approx 110$, and hence is similar to water. The TiO_2 was prepared by both slip and tape casting. Compositional modifications included additions of a glassy phase.

A. Slip Cast Dielectrics

The fabrication of dielectrics with dimensions on the order of a meter rules out many processing techniques, hence slip casting was initially pursued. Through a series of rheological studies, an optimized slurry suitable for slip casting was developed: 50 vol% TiO_2 , 0.25 wt% PVA based on solids (binder for green strength), 0.8 mg/m^2 Darvan C (dispersant) and a $\text{pH} \approx 10$ (electrostatic dispersion). This slurry was cast into large disks (up to $10''$ diameter) using plaster-of-paris molds, sintered to $\approx 97\%$ density at 1400°C - 6 h, and then planar-lapped to a $12 \mu\text{in}$ finish.

B. Tape Cast Dielectrics

Tape cast dielectrics were fabricated by doctor blading a slurry of 50 vol% TiO_2 dispersed in a nonaqueous binder system (MSI Ferro, CA.) Individual tape layers were 0.20 mm thick. Multilayer structures were fabricated by screen printing tapes with a Pt thick film ink, followed by lamination up to the desired thickness. Structures were dried for 5 days at 140°C , and calcined at 450°C for 5 days ($1^\circ\text{C}/\text{min}$ heating rate). Sintering was performed at varying temperatures to vary the grain size and density.

C. Glass Composites

The target microstructure has a 0-3 connectivity; i.e. a continuous, glassy grain boundary surrounding TiO_2 grains. A useful glassy phase needs to exhibit several key properties, including: a) the glass must "wet" the dielectric, but not react with it in a fashion detrimental to the electrical properties, b) the glass must result in higher densities, and c) the glass must exhibit a high electrical

* Operated for the United States Department of Energy under contract #DE-AC04-76-DP00613

Report Documentation Page			Form Approved OMB No. 0704-0188	
<p>Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p>				
1. REPORT DATE JUN 1999	2. REPORT TYPE N/A	3. DATES COVERED -		
4. TITLE AND SUBTITLE High Breakdown Strength, Multilayer Ceramics For Compact Pulsed Power Applications			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Missouri-Rolla, Rolla, Missouri, USA		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited				
13. SUPPLEMENTARY NOTES See also ADM002371. 2013 IEEE Pulsed Power Conference, Digest of Technical Papers 1976-2013, and Abstracts of the 2013 IEEE International Conference on Plasma Science. Held in San Francisco, CA on 16-21 June 2013. U.S. Government or Federal Purpose Rights License.				
14. ABSTRACT Advanced ceramics are being developed for use in large area, high voltage devices in order to achieve high specific energy densities (>106 J/m³) and physical size reduction. Initial materials based on slip cast TiO_x exhibited a high bulk breakdown strength (BDS ~300 kV/cm) and high permittivity with low dispersion (~100). However, strong area and thickness dependencies were noted. To increase the BDS, multilayer dielectric compositions are being developed based on glass/TiO_x composites. The addition of glass increases the density (~99.8% theoretical), forms a continuous grain boundary phase, and also allows the use of high temperature processes to change the physical shape of the dielectric. The permittivity can also be manipulated since the volume fraction and connectivity of the glassy phase can be readily shifted. Results from this study on bulk breakdown of TiOZ multilayer structures with an area of 2cm² and 0.1 cm thickness have measured 650 kV/cm. Furthermore, a strong dependence of breakdown strength and permittivity has been observed and correlated with microstructure and the glass composition. This paper presents the interactive effects of manipulation of these variables.				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF: a. REPORT unclassified			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 4
b. ABSTRACT unclassified			c. THIS PAGE unclassified	
19a. NAME OF RESPONSIBLE PERSON				

resistivity, as well as a high electrical breakdown strength. Borosilicate glasses were chosen for these reasons [1]. Table I summarizes the composition and properties of glasses made by melt fining and quenching. Volume fractions of these glasses ranging from 5-20% were added to the TiO_2 by ball milling, and then microstructural evolution studies were performed to optimize the density and minimize the grain size. Test specimens were tape cast as described above.

Table I. Properties of the Candidate Glasses

Glass	Comp.	T_m (°C)	Density (g/cc)	ρ ($\Omega\text{-cm}$)	K	BDS (V/mil)	ϕ
B	$\text{SiO}_2\text{-B}_2\text{O}_3$	1200	2.06	$\geq 10^{16}$	4	1900	58°
C	$\text{SiO}_2\text{-B}_2\text{O}_3$ CaO	1000	2.72	$\approx 10^{15}$	8.5	2060	8°
D	$\text{SiO}_2\text{-B}_2\text{O}_3$ CaO, Al_2O_3	1100	2.18	$\approx 10^{14}$	4	>1900	28°

III. RESULTS AND DISCUSSION

A. Slip Cast Titania

Initial studies focused on the influence of dielectric thickness and area on the breakdown strength of slip cast TiO_2 . This approach was pursued in the interest of ultimately producing 1 m diameter components. For example, Figure 1 shows an 8" diameter test specimen with sputtered-Au electrodes. To explore thickness effects on the D.C. breakdown strength, 1.25 cm diameter test specimens with a 0.25 cm hemispherical cathode and a planar anode were used. All measurements were performed in silicon oil. Figure 2 exhibits the results. Clearly the intrinsic breakdown strength of the dielectric is on the order of 750 kV/cm, but as a larger volume is stressed the breakdown strength decreased. A series of studies on the relationship between the microstructure and BDS led to the conclusion that the critical flaw size leading to this thickness dependency was on the order of 25 - 50 μm . These samples were all $\approx 96\%$ dense, hence the presence of even 4 vol% porosity did not seriously impact the BDS. Using results from Gerson [5] we might expect that the intrinsic BDS would be $\approx 25\%$ higher for 100% dense samples. The high grain boundary mobility

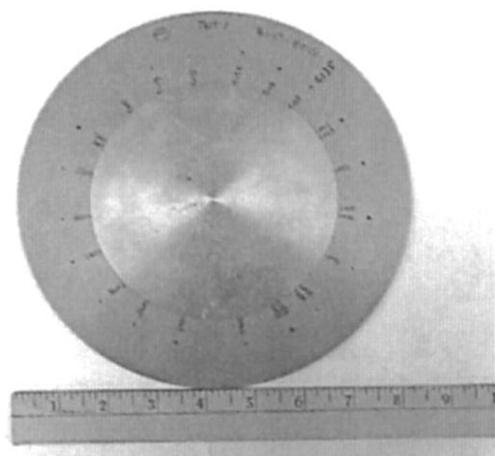


Figure 1. Slip cast TiO_2 dielectric.

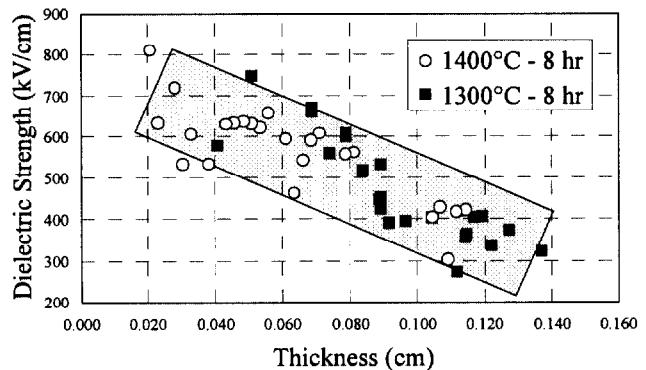


Figure 2. BDS as a function of dielectric thickness for slip cast TiO_2 .

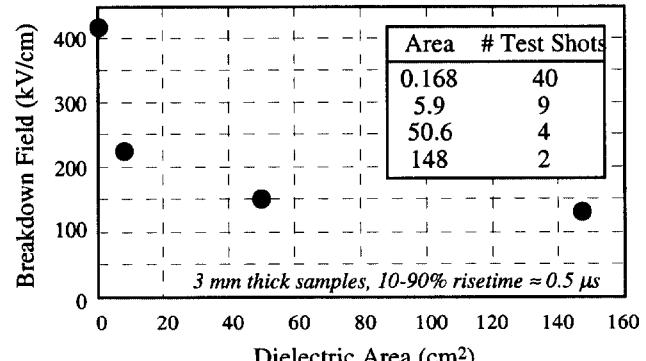


Figure 3. BDS as a function of electrode area for slip cast TiO_2 dielectrics.

of TiO_2 at these temperatures leads to mostly intragranular, spherical porosity. Spherical, 3 μm pores obviously do not strongly degrade the BDS.

Figure 3 shows the effect of stressed area on the BDS, using 0.3 cm thick planar samples as shown in Figure 1. Similar to the thickness dependency, larger area samples had significantly lower BDSs. Ultimately, the BDS appeared to be ≈ 100 kV/cm for larger area, thick parts. This was deemed unsuitable for the purposes of the desired pulsed power components.

B. Tape Cast Titania with Glass Phase Additions

1) Microstructural Evolution

The ability to fabricate a dense, composite dielectric with a glassy grain boundary is predicated on the ability of the glass to wet the dielectric. Table I contains the contact angle of the various glasses on TiO_2 taken from the SEM micrographs shown in Figure 4. Glass C wets the best, followed by the D and C glasses. All three can be used to create a continuous grain boundary phase, depending upon the volume fraction (V_f) of glass which is added. For instance, Figures 5 and 6 show SEM micrographs of 5 and 10 vol% additions of B glass. The 5 vol% addition resulted in a high density, but a discontinuous glass phase. Comparatively, the 10 vol% addition resulted in a nearly model microstructure, with virtually no porosity, and a continuous glassy grain boundary with a uniform thickness. The grain size is substantially larger, which is not as desirable in terms of ultimate BDS.

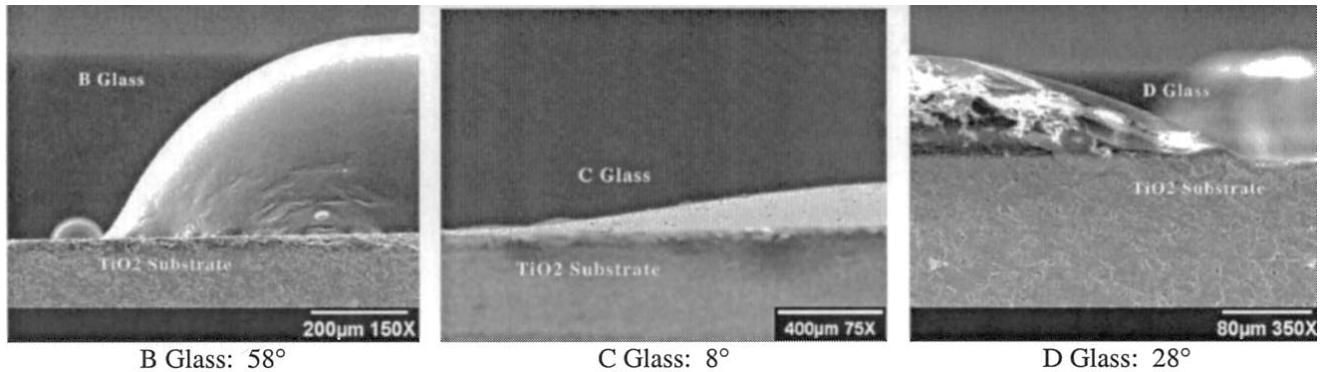


Figure 4. SEM micrographs of the wetting angle of glass droplets fired onto the TiO_2 dielectric.

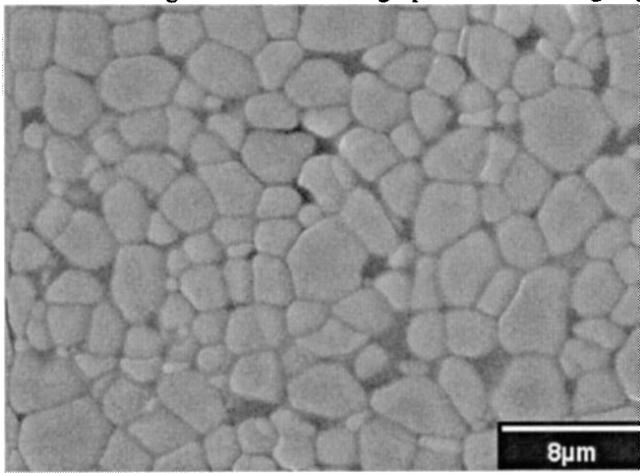


Figure 5. SEM micrograph of a TiO_2 dielectric with 5 vol% B glass additions.

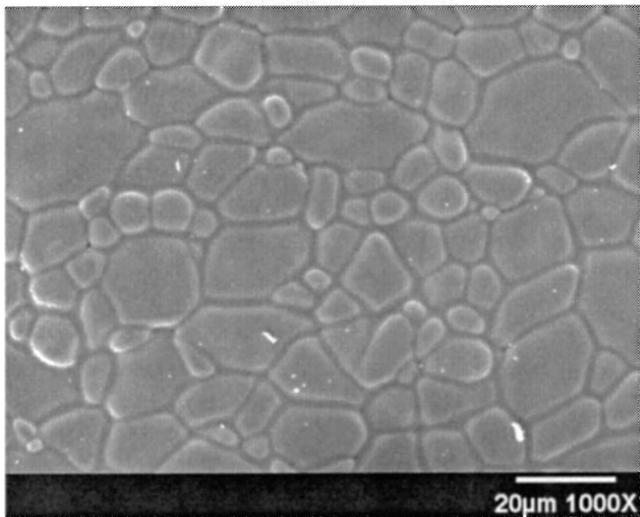


Figure 6. TiO_2 dielectric with 10 vol% B glass additions.

2) Electrical Properties

Certainly the presence of a low K glass in the grain boundary will decrease the overall K, the extent of which will depend on the V_f and thickness of the glassy grain boundary. Figure 7 exhibits the variation in K with V_f of the B glass. Pure TiO_2 has a $K \approx 110$. Additions of up to 20 vol% decreased the K to $\approx 70\text{--}85$, depending upon the soak time. Longer sintering times increases the grain size

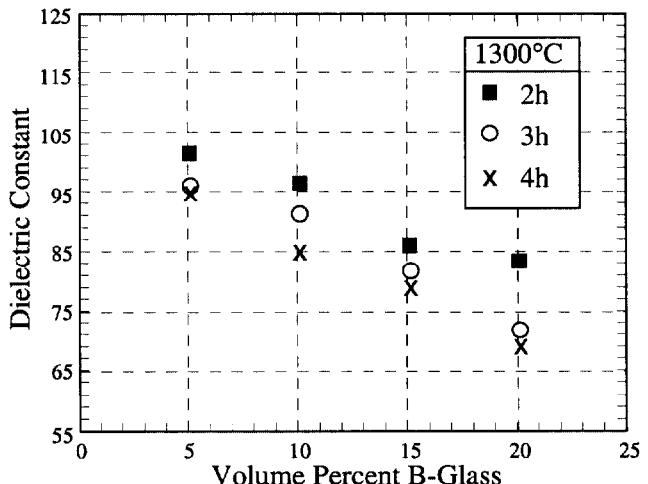


Figure 7. Effect of volume percent B-glass on the K.

and the thickness of the glassy grain boundary, resulting in an overall lower K.

The ultimate purpose of this investigation was to study the influence of a glassy grain boundary on the BDS. Table II summarizes the BDS results for all three glasses as a function of volume fraction and soak time at 1300°C, along with pure TiO_2 for comparison. These results can be summarized as follows:

- ◆ Compared to pure TiO_2 , all three glasses yielded higher BDSs. This is attributable to the higher densities which were achieved and the uniform microstructures.
- ◆ The BDS tracked closely with the density \rightarrow higher densities yielded higher BDSs, although exceptions exist due to changes in the grain size. For the most part, the 10 vol% samples exhibited the highest BDSs.
- ◆ In this study the D glass yielded the best properties, with a $BDS \approx 1650 \text{ V/mil}$ (650 kV/cm). This is very encouraging, and ongoing studies are focused on understanding why this composition yielded the highest BDS. This result cannot be explained on the basis of any fundamental glass properties or the resultant microstructures (which were similar between specimens).

Figure 8 graphically depicts the variation in BDS with soak time for the B glass. The maximum exhibited by the glasses occurs at the point where the density is a maximum, and the grain size is a minimum. Longer soak

Table II. Influence of Processing Conditions on the Breakdown Strength and Density of the Tape Cast TiO_2 Dielectrics

	1 hour		2 hour		3 hour		4 hour		6 hour		
	ρ (%)	BDS V/mil									
Pure TiO_2	89.1	590	92.5	895			94.0	770			
1% ZrO_2	89.2	810	91.6	1060			95.4	950			
B Glass	5%	92	994	94.7	1041	95.7	1114	96.5	1184	97.6	983
	10%	94	1006	97	994	97.7	1039	98.4	965	98.7	959
	15%	95.8	1285	98.8	1107	98.5	1054	99.4	1317	99.8	919
	20%	93.3	779	97.6	1072	99	1273	99.4	904	99.8	1033
C Glass	5%	95.5		96.5	976			97.1	874		
	10%	98.6	1128	97.7	1192			98.3	628	98.7	215
	15%	97.9		99.6	1113			99.8			
	20%	97.4		99.1	1016			99.8			
D Glass	5%	94.6		96.8	1140			98.3			
	10%	97.1	1006	98.7	1650			97.7	1290	98.8	1342
	15%	99.8		99.0	1162			99.3	1256		
	20%	99.8	1068	99.8	1167			99.8	1246		

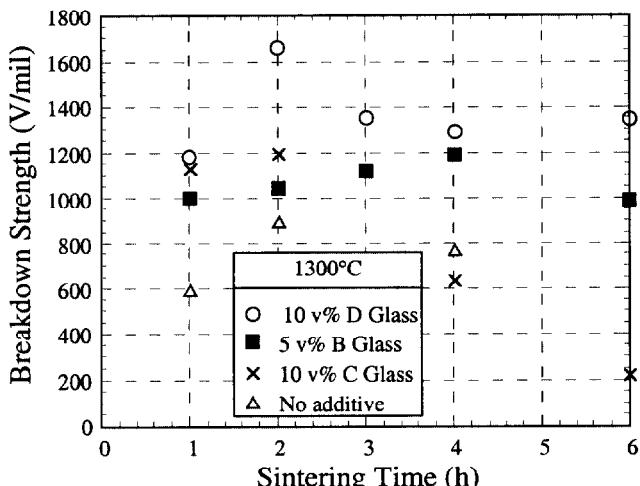


Figure 8. Effect of sintering soak time on the BDS.

times result in larger grains, and hence a larger critical flaw size which controls the BDS.

C. Multilayer Structures

Recent work on multilayer structures has indicated that the presence of interleaving layers of a continuous metallic film within a dielectric increases not only its bulk breakdown strength, but also the surface flashover voltage. This structure is called the "Ultrahigh Gradient Insulator." Tape casting can readily be used to produce 2-2 structures, hence work is underway to incorporate the glass-loaded systems into this configuration. Figure 9 shows the first insulator produced in this manner; this insulator has 25 layers of TiO_2 with internal Pt electrodes. No electrical tests have been performed as of this writing.

IV. SUMMARY

Through modification of the microstructure with glass phase additions the bulk BDS of titania dielectrics has been substantially increased. The addition of glass increases the density, forms a continuous grain boundary phase, and allows for systematic control of the

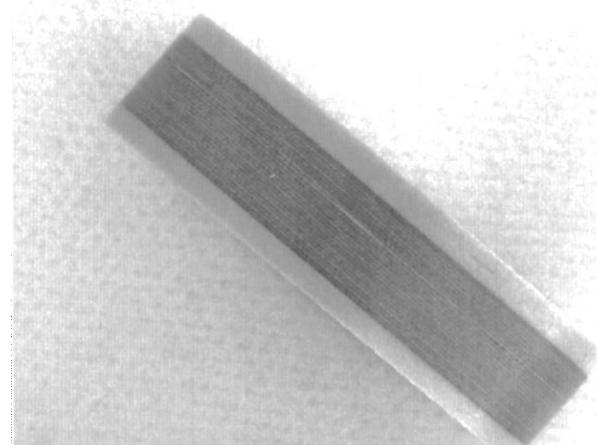


Figure 9. 1.1" diameter, multilayer TiO_2 with 25 layers of Pt internal electrodes.

permittivity. The energy density of these dielectrics is on the order of 1 MJ/m³, and as such show great promise for compact pulsed power applications.

V. REFERENCES

- [1] S.T. Pai and Q. Zhang, Introduction to High Power Pulse Technology, World Scientific Publishing Co., Singapore.
- [2] Z. Deheng and Y. Zhang, High Voltage Electrical Insulation, Tsinghua University Press, Beijing (1992).
- [3] I.O. Owate and R. Freer, "Dielectric breakdown of ceramics and glass ceramics," in Proc. 6th Intl Conf. on Dielectric Materials, Measurements and Applications, 1992, p. 443.
- [4] R. Gerson and T.C. Marshall, "Dielectric Breakdown of Porous Ceramics," *J. Appl. Phys.*, vol. 30, pp. 1650-1653, Nov. 59.
- [5] G. Economos, "The Effect of Microstructure on the Electrical and Magnetic Properties of Ceramics," Ceramic Fabrication Processes, W.D. Kingery, Ed., New York, John Wiley & Sons, 1950, pp. 201-213.